

CHAPTER 2

Presentation of Solubility Data: Units and Applications

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The solubility of gases in water and other aqueous media such as seawater and more concentrated solutions is central to the description of the uptake and reactions of these gases in aerosols, precipitation, surface water and other aqueous media such as the intracellular fluids of plants and animals. It is also pertinent to sampling of soluble atmospheric gases in aqueous medium for analytical purposes. This book presents evaluated summaries of data pertinent to the solubility of gases in aqueous media. This chapter introduces the terminology by which this solubility is described and the pertinent units and presents examples of applications pertinent to atmospheric chemistry. As is seen below, a variety of units have been and continue to be employed for gas solubility data, so some attention must be given to this subject. As this is an IUPAC publication, every effort is made to employ units that are consistent with the International System of Units (Système International, SI) [1]. However, in IUPAC publications of solubility data it is usual to publish data in the original units in addition to SI units. The consistency of SI makes this system of units convenient for application in atmospheric chemistry and related disciplines [2]. However, as elaborated below, there are some departures from strict SI that persist in chemical thermodynamics that require special consideration.

The solubility of weakly soluble gases in liquids is one of the oldest branches of physical chemistry. The origins of this study go back to William Henry (1775–1836), whose presentation before the Royal Society and subsequent publication [3] gave rise to what has come to be known as Henry's law. That paper describes a series of experiments with several gases which remain of concern to present-day atmospheric scientists, CO₂, H₂S, N₂O, O₂, CH₄, N₂, H₂, CO and PH₃. The gas and liquid were contacted and allowed to reach solubility equilibrium at various values of applied pressure, with the amount of absorbed

gas determined from the decrease in gaseous volume after equilibration with the water. The generalization reached by Henry is stated in the original paper as follows:

The results of a series of at least fifty experiments on [the several gases] establish the following general law: *that under equal circumstances of temperature, water takes up, in all cases, the same volume of condensed gas [at higher applied pressure] as of gas under ordinary pressure.* But as the spaces [volumes] occupied by every gas are inversely as the compressing force [pressure], it follows, *that water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice &c. the volume absorbed under the common pressure of the atmosphere.* [italics in original]

In other words, the amount of gas absorbed, as measured by volume at ordinary pressure, is proportional to the applied pressure.

It is also clear in the presentation that Henry realized that the amount of dissolved material (extensive property) scaled linearly with the amount of water; in fact, Henry normalized his results to a standard amount of water, so that it is clear that he recognized that it is the concentration (intensive property) that is proportional to the pressure of the gas.

In a subsequent appendix, Henry [4] noted that the residuum of undissolved gas was not always entirely pure and exhibited an increasing proportion of less soluble contaminant, necessitating correction of his originally presented data. He states in this connection:

For, the theory which Mr. DALTON has suggested to me on this subject, and which appears to be confirmed by my experiments, is, that the absorption of gases by water is a purely a mechanical effect, and that its amount is exactly proportional to the density of the gas, considered abstractedly from any other gas with which it may accidentally be mixed. Conformably to this theory, if the residuary gas contain 1/2, 1/10, or any other proportion, of foreign gas, the quantity absorbed by water will be 1/2, 1/10, &c. short of the maximum.

In this elaboration, Henry makes use of Dalton's newly enunciated law of partial pressures to correct his previously reported data.

This brief summary of these experiments permits us to restate Henry's law with complete fidelity to his original formulation, changing only the terminology, as follows: the equilibrium concentration of a dissolved gaseous species is proportional to the partial pressure of the gas, the proportionality constant being a property of the gas and a function of temperature, or

$$[X(aq)] = k_{H_X}(T)p_X \quad (2.1)$$

where $[X(aq)]$ is the aqueous concentration, p_X is the gas-phase partial pressure and $k_{H_X}(T)$ is the Henry's law coefficient of the gas X in water at temperature T .

The law is readily generalized to other solvents, the Henry's law coefficient depending on both the solvent and the solute, to mixed solvents, and to solvents

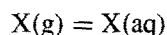
containing nonvolatile solutes. In the terminology of modern physical chemistry, Henry's law is a limiting law:

$$k_{H_X} = \lim_{p_X \rightarrow 0} \frac{[X(aq)]}{p_X}$$

the reason being that the properties of the solvent change with increasing concentrations of solute. This situation can be accounted for by expressing Henry's law in terms of the activities in the pertinent phases:

$$a_{X(aq)} = k_{H_X}(T) a_{X(g)}$$

We thus observe that the Henry's law coefficient is an equilibrium constant for the reaction



Recognition of this leads to an intrinsic connection to chemical thermodynamics, and in particular to the fact that the Henry's law coefficient is related in the customary way to the free energy change of reaction as

$$k_{H_X} = \exp(-\Delta G^\circ / RT)$$

where in this case ΔG° is the free energy of dissolution:

$$\Delta G^\circ = \Delta_f G^\circ(X_{aq}) - \Delta_f G^\circ(X_g)$$

the $\Delta_f G^\circ$'s being the standard free energies of formation of the aqueous and gaseous species. In practice, it is the usual situation that knowledge of the Henry's law coefficient allows one to determine the unknown standard free energy of formation of one of the two species from the known value for the other, rather than the Henry's law coefficient being calculated from two known standard free energies of formation. However, there are important practical exceptions in instances of highly reactive gases whose reactivity precludes establishment of the solubility equilibrium at measurable concentration and partial pressure.

The reason for focusing here on Henry's law and for quoting from Henry's original paper is in part to provide justification for the form of Henry's law employed in the present work, and advocated for universal use, namely that it is the aqueous-phase concentration (or, alternatively, molality) that is viewed as proportional to the gas-phase partial pressure, rather than the other way around, as has been a customary expression of Henry's law by many subsequent investigators in the nearly 200 years since Henry's initial report. From the perspective of the atmospheric scientist, this approach has a certain further justification as well: it is usually the gas-phase partial pressure that can be considered the independent or controlling variable, with the aqueous-phase concentration dependent on the gas-phase partial pressure. Henry's law is the basis for any consideration of exchange of material between the gas phase and natural waters, and the Henry's law coefficient is central to expressions that describe the extent and rate

of such exchange, even for species whose equilibrium solubility is not adequately described by Henry's law.

It must be stressed that expressing Henry's law according to Equation (2.1) is by no means universal either in the physical chemistry literature or in the environmental sciences. Frequently it is customary to express Henry's law the other way around (gas-phase partial pressure proportional to aqueous-phase concentration); this can even be sometimes more convenient, as in considerations of the evasion of dissolved gases from solution, as from a lake to the atmosphere. In any event, it is inevitable to encounter Henry's law expressed in this reverse sense. Also, a variety of modes of expression have been employed for describing the concentration of dissolved gas, such as the volume that it would occupy at a standard pressure, or mole fraction relative to solvent, that have led to yet further variants of Henry's law and to tabulations of Henry's law coefficients in a multiplicity of units. It is thus imperative, at the present time and for the foreseeable future, to pay attention to the sense and units of Henry's law as employed by different investigators and to convert Henry's law coefficients from one set of units (and sense of the law) to another. Consequently, we address these issues in this chapter and present algorithms for and examples of such conversions. As noted above, there is a further desire to employ SI units, and the consequent necessity for making the use of these units more familiar and for dealing with special problems associated with the fact that the units conventions of chemical thermodynamics are not entirely consistent with SI.

For a detailed review of modeling interactions between gaseous species and liquid water in the atmosphere, see Sander [5].

1 UNITS

As a measure of aqueous-phase abundance we employ molality, the mixing ratio of the solute in the solution, having unit mole of solute per kg of solvent, mol kg^{-1} . Use of this measure and unit is consistent with current practice in chemical thermodynamics and is preferred to concentration, which, because of density change associated with temperature change, is not constant with temperature for a solution of a given composition. Nonetheless, concentration is commonly employed, with the most common unit being molar (moles per litre of solution, mol l^{-1} or M). This unit suffers from the further disadvantage that the litre is not an SI unit, the SI unit of volume being the cubic meter. In practice, because the mass of 1 l of water is approximately equal to 1 kg, the molality of a dilute aqueous solution is approximately equal numerically to the molar concentration. More precisely, for a single component solution, the concentration of a solute X, C_X , is related to the molality of the solute m_X as

$$C_X \left(\frac{\text{mol}_{\text{solute}}}{\text{l}_{\text{solution}}} \right) = m_X \left(\frac{\text{mol}_{\text{solute}}}{\text{kg}_{\text{solvent}}} \right) \times \rho_{\text{solvent}} \left(\frac{\text{kg}_{\text{solvent}}}{\text{l}_{\text{solution}}} \right) \quad (2.2)$$

where ρ_{solvent} denotes the density of the solvent in the solution:

$$\rho_{\text{solvent}} = \frac{\rho_{\text{solution}}}{1 + \text{MW}_X m_X}$$

where ρ_{solution} denotes the solution density and MW_X denotes the molar mass (molecular weight) of species X, in units of kg mol^{-1} . More generally, for a multicomponent solution,

$$\rho_{\text{solvent}} = \frac{\rho_{\text{solution}}}{1 + \sum_i \text{MW}_{X_i} m_{X_i}} \quad (2.3)$$

where the summation is taken over all solutes. For dilute aqueous solutions the solvent density is nearly equal to 1 kg mol^{-1} , so the concentration and molality are numerically essentially equal, i.e.

$$C_X \left(\frac{\text{mol}_{\text{solute}}}{\text{l}_{\text{solution}}} \right) \approx m_X \left(\frac{\text{mol}}{\text{kg}_{\text{solvent}}} \right) \left\{ \times 1 \left(\frac{\text{kg}_{\text{solvent}}}{\text{l}_{\text{solution}}} \right) \right\} \quad (2.4)$$

where the quantity in braces can be omitted for numerical work but must be retained for units calculus. For more concentrated solutions of importance in atmospheric chemistry, such as aqueous clear-air aerosol, including sea salt, or for stratospheric sulfuric acid aerosol, the volume fraction of solute and the resulting departure from unit solvent density can be appreciable.

Where sufficient pressure dependence data are available to report the Henry's law coefficient as a limiting law, then that value is reported, i.e.

$$k_{H_X} (\text{mol kg}^{-1} \text{ bar}^{-1}) \equiv \lim_{p_X \rightarrow 0} \frac{m_X (\text{mol kg}_{\text{solvent}}^{-1})}{p_X (\text{bar})}$$

When such data are not available (which is generally the situation), the Henry's law coefficient is reported as the quotient of molality by partial pressure, with the partial pressure (range) of the measurements specified:

$$k_{H_X} (\text{mol kg}^{-1} \text{ bar}^{-1}) = \frac{m_X (\text{mol kg}_{\text{solvent}}^{-1})}{p_X (\text{bar})}$$

For application in atmospheric chemistry, the lack of such pressure-dependent data should make little practical difference provided that there are good reasons to assume that the measurements were made within a pressure range in which Henry's law is applicable. This means that linear extrapolation to zero pressure would correspond to zero concentration.

Solubility data are reported at the temperature(s) of measurement. Where sufficient temperature-dependence data are available, the enthalpy change of solution is reported as

$$\frac{\Delta H^\circ}{R_g} = - \frac{d \ln(k_{H_X} / 1 \text{ mol kg}^{-1} \text{ bar}^{-1})}{d(1/T)}$$

In principle, this quantity can also be obtained from the limiting-law solubility data, but again in practice such data are not generally available, again a situation of little practical consequence.

The unit $\text{mol kg}^{-1} \text{ bar}^{-1}$ for the Henry's law coefficient is practical for many applications, generally, and specifically in atmospheric chemistry, with the obvious proviso that the partial pressure of the gas be expressed in units of bar.

We adopt the symbol k_H for this practical quantity, and likewise employ the symbol p_X to denote the partial pressure in bar of the species X. However, as these units are not products of powers of base SI units, their use leads to complications, especially in expressions in which they are combined with SI quantities. It is necessary to employ a Henry's law coefficient in SI units in such expressions, which we distinguish by a caret, \hat{k}_H , where $\hat{k}_H = 10^{-5}k_H$. Likewise to avoid ambiguity, when we employ partial pressure in pascals, we use the symbol \hat{p}_X .

Increasingly the mixing ratio x_X is gaining favour in atmospheric chemistry as the quantity for expressing local abundance; units are mol/mol (air), e.g. nmol/mol. Since Henry's law solubility depends on the partial pressure of the gas, rather than mixing ratio, it is necessary to 'convert' from mixing ratio to partial pressure. This is readily achieved as

$$p_X(\text{bar}) = p(\text{bar})x_X(\text{mol/mol})$$

so that

$$m_X(\text{mol kg}_{\text{solvent}}^{-1}) = k_{H_X}(\text{mol kg}^{-1}\text{bar}^{-1})p(\text{bar})x_X(\text{mol/mol})$$

In many applications, such as the evaluation of chemical kinetics and mass transport rates, the concentration is required, rather than the molality, and it is therefore often convenient to employ a Henry's law coefficient that yields the concentration directly. If we denote this concentration Henry's law coefficient H_X (units M bar^{-1}), then within the approximation that the solvent density is equal to 1 kg mol^{-1} ,

$$H_X \left(\frac{\text{M}}{\text{bar}} \right) \approx k_{H_X} \left(\frac{\text{mol kg}^{-1}}{\text{bar}} \right) \left\{ \times 1 \left(\frac{\text{kg}_{\text{solvent}}}{\text{l}_{\text{solution}}} \right) \right\} \quad (2.5)$$

In many considerations of mass transport it is useful to employ a dimensionless Henry's law coefficient, the ratio of concentration in solution (aqueous) phase to that in the gas phase (or vice versa; extreme caution is suggested in using dimensionless Henry's law coefficients because the sense of the equilibrium cannot be inferred from the units of the quantity). We take this dimensionless Henry's law coefficient also in the sense aqueous/gaseous:

$$\tilde{H}_X \equiv \frac{C_{X(\text{aq})}(\text{mol m}^{-3})}{C_{X(\text{g})}(\text{mol m}^{-3})}$$

where the dimensionless property is denoted by the tilde over the symbol. Within the accuracy of the ideal gas law (adequate for all practical purposes in atmospheric chemistry, at least on earth), the concentration (mol m^{-3}) of a gaseous species X having partial pressure \hat{p}_X (Pa) is given as

$$C_{X(\text{g})} = \hat{p}_X / R_g T$$

where R_g is the universal gas constant and T is the absolute temperature. From Equation (2.2) the aqueous-phase concentration of the dissolved gas (mol m^{-3}) is

$$C_{X(\text{aq})} \left(\frac{\text{mol}}{\text{m}^3_{\text{solution}}} \right) = \hat{k}_{H_X} \left(\frac{\text{mol kg}_{\text{solvent}}^{-1}}{\text{Pa}} \right) \hat{p}_X(\text{Pa}) \rho_{\text{solvent}} \left(\frac{\text{kg}_{\text{solvent}}}{\text{m}^3_{\text{solution}}} \right)$$

Both the aqueous and gaseous concentrations scale with partial pressure; the ratio of these quantities, the dimensionless Henry's law coefficient, is of course independent of partial pressure:

$$\tilde{H}_X = \hat{k}_{H_X} \left(\frac{\text{mol kg}_{\text{solvent}}^{-1}}{\text{Pa}} \right) \rho_{\text{solvent}} \left(\frac{\text{kg}_{\text{solvent}}}{\text{m}^3_{\text{solution}}} \right) R_g \left(\frac{\text{Pa m}^3}{\text{mol K}} \right) T(\text{K}) \quad (2.6)$$

For all quantities on the right-hand side of Equation (2.6) in strict SI units the quantity $\hat{k}_{H_X} \rho_{\text{solvent}} R_g T(\text{K})$ is a dimensionless group. This expression exhibits its simple form as a direct consequence of employing consistent units, specifically the Henry's law coefficient in units of $\text{mol kg}_{\text{solvent}}^{-1} \text{Pa}^{-1}$. Note that for dilute aqueous solution the solvent density ($\text{kg}_{\text{solvent}} \text{m}_{\text{solution}}^{-3}$) has a value of approximately $10^3 \text{ kg}_{\text{solvent}} \text{m}_{\text{solution}}^{-3}$.

For the Henry's law coefficient given in units of $\text{mol kg}_{\text{solvent}}^{-1} \text{bar}^{-1}$, a conversion factor must be applied:

$$\tilde{H}_X = 10^{-5} \left(\frac{\text{bar}}{\text{Pa}} \right) k_{H_X} \left(\frac{\text{mol kg}_{\text{solvent}}^{-1}}{\text{bar}} \right) \rho_{\text{solvent}} \left(\frac{\text{kg}_{\text{solvent}}}{\text{m}^3_{\text{solution}}} \right) R_g \left(\frac{\text{Pa m}^3}{\text{mol K}} \right) T(\text{K})$$

For solvent density expressed in units of $\text{kg}_{\text{solvent}} \text{l}_{\text{solution}}^{-1}$, this becomes

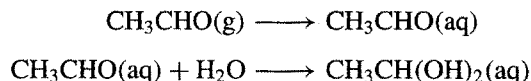
$$\begin{aligned} \tilde{H}_X &= 10^{-2} k_{H_X} \left(\frac{\text{mol kg}_{\text{solvent}}^{-1}}{\text{bar}} \right) R_g \left(\frac{\text{Pa m}^3}{\text{mol K}} \right) T(\text{K}) \rho_{\text{solvent}} \left(\frac{\text{kg}_{\text{solvent}}}{\text{l}_{\text{solution}}} \right) \\ &\approx 10^{-2} k_{H_X} R_g T \end{aligned}$$

where the final approximate equality holds within the approximation of the solvent density equal to 1 kg l^{-1} . The conversion factors are a direct consequence of use of inconsistent units. For this reason, use of strict SI units for the Henry's law coefficient ($\text{mol kg}_{\text{solvent}}^{-1} \text{Pa}^{-1}$) is to be preferred where this quantity is combined with others in algebraic expressions.

2 AQUEOUS-PHASE SOLUBILITY EQUILIBRIA

Before proceeding, we should note an important qualification to Henry's law, namely that it applies to sparingly soluble gases or, more precisely, to gases which are physically dissolved but not undergoing chemical reaction in solution to form a chemically different species. Here physical absorption includes solvation but does not include reaction to form a distinct chemical species, such as hydration.

For example, the dissolution of acetaldehyde can be represented by the following sequence of reactions:



The first of these is physical dissolution, i.e. the Henry's law equilibrium; the second is a chemical reaction. The pertinent equilibrium expressions are:

$$k_{\text{HCH}_3\text{CHO}} = \frac{[\text{CH}_3\text{CHO}(\text{aq})]}{p_{\text{CH}_3\text{CHO}}}$$

and

$$k_{\text{hydCH}_3\text{CHO}} = \frac{[\text{CH}_3\text{CH}(\text{OH})_2(\text{aq})]}{[\text{CH}_3\text{CHO}(\text{aq})]}$$

The total dissolved acetaldehyde concentration is evaluated as the sum of the two dissolved species:

$$\begin{aligned}[\text{CH}_3\text{CHO}(\text{aq, tot})] &= [\text{CH}_3\text{CHO}(\text{aq})] + [\text{CH}_3\text{CH}(\text{OH})_2(\text{aq})] \\ &= k_{\text{HCH}_3\text{CHO}} p_{\text{CH}_3\text{CHO}} (1 + k_{\text{hydCH}_3\text{CHO}})\end{aligned}$$

In practice, whether or not to include the hydrated species as a part of the dissolved component depends on the experiment or application and whether the dissolution process is rapid or slow compared with the hydration reaction or other possible reaction, such as reaction of H_2CO with dissolved S(IV). What is important to note for the present purpose is that the equilibrium concentration of the hydrated species is itself proportional to that of the unhydrated species, so that the total is proportional to the concentration of the unhydrated species and the overall linearity between gas-phase partial pressure and aqueous concentration is retained. One can take advantage of this linearity to define an effective Henry's law coefficient, in this instance

$$k_{\text{HCH}_3\text{CHO}}^* \equiv k_{\text{HCH}_3\text{CHO}} (1 + k_{\text{hydCH}_3\text{CHO}})$$

such that one has for the total dissolved acetaldehyde concentration an expression that is formally identical with Henry's law, viz.

$$[\text{CH}_3\text{CHO}(\text{aq, tot})] = k_{\text{HCH}_3\text{CHO}}^* p_{\text{CH}_3\text{CHO}}$$

It is of course crucial in any potentially ambiguous situation to specify whether the Henry's law coefficient refers to the total or only to the unhydrated species. This is important also in correlations of Henry's law coefficients with chemical structure. Physical solubility depends on properties such as polarizability, which depend on molecular structure and number of electrons; correlations based on such properties can obviously be disrupted if there is a structural change associated with the hydration.

Much important in this context is the exclusion from the rubric of Henry's law any chemical reaction that results in a solubility that is not linear in the partial pressure of the gaseous species. Consider the solubility equilibrium for the dissolution of the strong acid HCl:



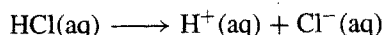
for which the equilibrium relation is

$$k_{\text{eq}} = \frac{[\text{H}^+][\text{Cl}^-]}{p_{\text{HCl}}}$$

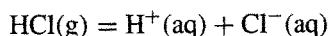
For both H^+ and Cl^- deriving entirely from the dissolved hydrochloric acid, which may be considered entirely dissociated, then

$$p_{\text{HCl}} = k_{\text{eq}}^{-1} [\text{Acid}]^2$$

where [Acid] denotes the aqueous concentration of the dissolved acid, a nonlinear relation, and *ipso facto*, not Henry's law (here we have considered the aqueous acid concentration to be the independent variable, consistent with the fact that virtually all the material would be present in solution, rendering this concentration the more readily measured variable). For a variety of reasons such as description of mass transport rates it may be useful to consider the actual Henry's law constant of HCl. Formally this is related to the overall equilibrium constant k_{eq} through the sequence of reactions



which sum to give the overall reaction



Correspondingly, the equilibrium expressions are

$$k_{\text{H}_{\text{HCl}}} = \frac{[\text{HCl(aq)}]}{p_{\text{HCl}}}$$

$$k_{\text{a}} = \frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl(aq)}]}$$

and

$$k_{\text{eq}} = \frac{[\text{H}^+][\text{Cl}^-]}{p_{\text{HCl}}}$$

where $k_{\text{H}_{\text{HCl}}}$ is the Henry's law coefficient for HCl, k_{a} is the acid dissociation constant of aqueous HCl and k_{eq} is the equilibrium constant for the overall reaction. If the overall equilibrium constant k_{eq} can be determined, by measurement of partial pressure and aqueous activities of the two ionic species, and if, generally

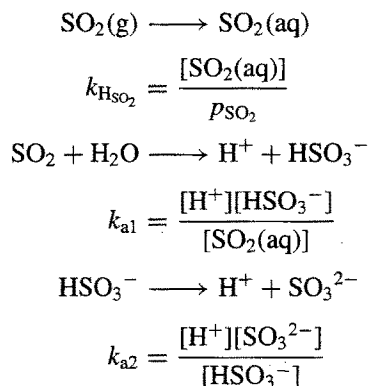
in a separate experiment, the acid dissociation constant K_a can be determined, then the Henry's law coefficient (equilibrium constant of physical solubility) of HCl can be evaluated as

$$k_{\text{HCl}} = k_{\text{eq}}/k_a$$

Where data are available to permit the determination of both the Henry's law coefficient and the equilibrium constant(s) of the pertinent aqueous-phase reaction(s), then all these data are presented. Frequently only the equilibrium constant for the overall reaction is known or, because of uncertainties in determination of the individual component equilibrium constants, it is known with greater accuracy. In that case the overall solubility equilibrium constant is presented, together with the enthalpy change associated with the overall reaction.

3 EFFECTIVE HENRY'S LAW COEFFICIENTS

In the case of a weakly acidic gas dissolving in an aqueous solution that may be considered well buffered relative to the incremental acidity resulting from dissolution of the gas, it may be possible to assume that the acid concentration is constant, in which case the total amount of dissolved gas is linear in the gas-phase partial pressure. Consider the dissolution of SO_2 :



For this system it is possible and convenient to define a pH-dependent effective Henry's law coefficient for total dissolved sulfur(IV):

$$k_{\text{HS(IV)}}^* \equiv k_{\text{H}\text{SO}_2} \left(1 + \frac{k_{a1}}{[\text{H}^+]} + \frac{k_{a1}k_{a2}}{[\text{H}^+]^2} \right)$$

such that under the assumption that the aqueous solution is well buffered one obtains a Henry's law-like expression for total dissolved sulfur(IV):

$$[\text{S(IV)}(\text{aq})] = k_{\text{HS(IV)}}^* p_{\text{SO}_2}$$

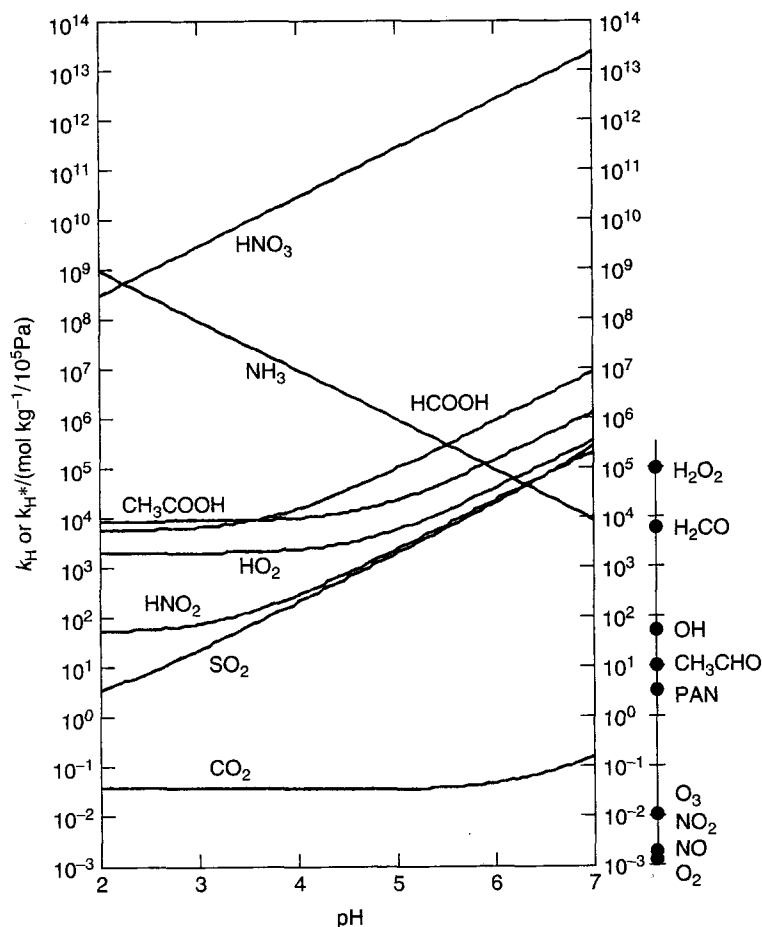


Figure 2.1 pH dependence of the effective Henry's law constant for gases which undergo rapid acid-base dissociation reactions in dilute aqueous solution, as a function of solution pH. The buffer capacity of the solution is assumed to exceed greatly the incremental concentration from the uptake of the indicated gas. Also indicated at the right of the figure are Henry's law constants for nondissociative gases. $T \approx 300 \text{ K}$ (modified from Schwartz [6]; for references, see Schwartz [7])

Expressions such as this have found much application in consideration of scavenging of gases by cloudwater and in considerations also of the coupled mass transport and chemical reaction in cloudwater. Figure 2.1 shows the pH dependence of the effective Henry's law coefficient for gases which undergo rapid acid-base dissociation reactions in dilute aqueous solution as a function of solution pH. Also shown for reference are the Henry's law coefficients of several nondissociative gases of atmospheric interest. Note the great increase in effective Henry's law coefficient resulting from the greater solubility of the ionic species than the parent neutral species.

4 PARTITION EQUILIBRIA IN LIQUID-WATER CLOUDS

The key initial characterization of the distribution of a volatile substance between gas and liquid phases in a cloud is the equilibrium distribution. This distribution depends in the first instance on the liquid water content of the cloud. Values of cloud liquid water content L are typically of the order of 1 g m^{-3} , i.e. $1 \times 10^{-3} \text{ kg m}^{-3}$. (The commonly used measure of liquid water content, the liquid water volume fraction, is related to L as L/ρ_{cw} , where ρ_{cw} the density of cloudwater is ca 1 kg m^{-3} ; the liquid water volume fraction is thus of the order of 1×10^{-6} .) For a volatile substance dissolving according to Henry's law, the amount of material per cubic meter in the aqueous phase is

$$n_{\text{X(aq)}} \left(\frac{\text{mol}}{\text{m}^3} \right) = L \left(\frac{\text{kg}}{\text{m}^3} \right) \hat{k}_{\text{Hx}} \left(\frac{\text{mol kg}^{-1}}{\text{Pa}} \right) \hat{p}_{\text{X}}(\text{Pa})$$

The amount of material per cubic meter in the gas phase is

$$n_{\text{X(g)}} = \hat{p}_{\text{X}}(1 - L/\rho_{\text{cw}})/R_g T \approx \hat{p}_{\text{X}}/R_g T \text{ for } L/\rho_{\text{cw}} \ll 1$$

The partition ratio, the ratio of material in the liquid to gas phase, is thus

$$\frac{n_{\text{X(aq)}}}{n_{\text{X(g)}}} = \frac{L \hat{k}_{\text{Hx}} \hat{p}_{\text{X}}}{\hat{p}_{\text{X}}/R_g T} = L \hat{k}_{\text{Hx}} R_g T$$

This result is readily extended to more complicated solution equilibria, especially through the use of the effective Henry's law coefficient.

Similar considerations pertain to the evaluation of the equilibrium distribution between air and an aqueous scrubbing solution employed in extracting a soluble gas from the atmosphere; here the liquid water volume fraction would be replaced by the ratio of flow-rates of solution to air.

Note that we have employed the strict SI version of the Henry's law coefficient having units, $\text{mol kg}^{-1} \text{ Pa}^{-1}$. Unfortunately, if we use the Henry's law coefficient in practical units, $\text{mol kg}^{-1} \text{ bar}^{-1}$, we must use a units conversion factor of $1 \times 10^{-5} \text{ bar Pa}^{-1}$:

$$\frac{n_{\text{X(aq)}}}{n_{\text{X(g)}}} = 10^{-5} \left(\frac{\text{bar}}{\text{Pa}} \right) L \left(\frac{\text{kg}}{\text{m}^3} \right) k_{\text{Hx}} \left(\frac{\text{mol kg}^{-1}}{\text{bar}} \right) R_g \left(\frac{\text{Pa m}^3}{\text{mol K}} \right) T(\text{K})$$

The partition ratio can be readily assessed from the value of the quantity $L \hat{k}_{\text{Hx}} R_g T$. For a given situation of liquid water content and temperature it is useful to consider the value of the Henry's law coefficient k_{H50} such that 50 % of the substance is in each phase:

$$\hat{k}_{\text{H50}} = (L R_g T)^{-1} \text{ or } k_{\text{H50}} = 10^5 (L R_g T)^{-1}$$

For scoping purposes, we note that for $T \approx 300 \text{ K}$, $R_g T \approx 2.5 \times 10^3 \text{ m}^3 \text{ Pa}/(\text{mol kg}^{-1})$, so that for $L \approx 1 \times 10^{-3} \text{ kg m}^{-3}$, $\hat{k}_{\text{H50}} \approx 0.4 \text{ mol kg}^{-1} \text{ Pa}^{-1}$ and $k_{\text{H50}} \approx 4 \times 10^4 \text{ mol kg bar}^{-1}$. Note that for most gases of atmospheric interest $k_{\text{H}} \ll k_{\text{H50}}$

so that the equilibrium distribution consists of virtually all of the substance present in the gas phase; a key exception is H_2O_2 . However, the effective Henry's law coefficient approaches or in some instances substantially exceeds $k_{\text{H}_{50}}$, for example HNO_3 , which at equilibrium is present virtually entirely in solution phase.

The fraction of the total volatile material that is present in the aqueous phase is

$$F_{\text{X(aq)}} = \frac{n_{\text{X(aq)}}}{n_{\text{X(g)}} + n_{\text{X(aq)}}} = \frac{10^{-5} L k_{\text{H}_\text{X}} R_g T}{1 + 10^{-5} L k_{\text{H}_\text{X}} R_g T}$$

For a weakly soluble gas such that $\hat{k}_{\text{H}_\text{X}} R_g T \ll 1$ (i.e. $10^{-5} L k_{\text{H}_\text{X}} R_g T \ll 1$),

$$F_{\text{X(aq)}} \longrightarrow \hat{k}_{\text{H}_\text{X}} R_g T = 10^{-5} L k_{\text{H}_\text{X}} R_g T$$

As noted above, the recurrence of the factor 10^5 is due to the standard state of gaseous substances being taken as 1 bar (rather than 1 Pa), which leads to the Henry's law coefficient k_{H_X} having the units $\text{mol kg}^{-1} \text{bar}^{-1}$, rather than $\text{mol kg}^{-1} \text{Pa}^{-1}$, which would be consistent with SI units.

5 EXPRESSIONS FOR ABUNDANCE OF MATERIALS IN MULTI-PHASE SYSTEMS

Frequently it is useful to compare on an equivalent basis the amounts of trace species present in a volume of air in different phases (gas, aqueous, particulate). A variety of quantities and units have been employed to express such abundances, as summarized by Schwartz and Warneck [2]. Use of mole based units is advocated whenever possible (known composition and molecular weight) because these units display chemically meaningful relationships. Because mixing ratio by volume is appropriate only for gas-phase species, this quantity is not suitable. Suitable quantities and units are concentration (mol m^{-3}), mixing ratio (mole per mole air) and equivalent partial pressure, the partial pressure that the species would exhibit if an ideal gas, \hat{p}_X^* (Pa) or p_X^* (bar). Of the several quantities, mixing ratio seems most general and suitable.

Consider a species X present in cloudwater (liquid water content $L \text{ kg m}^{-3}$) with molality $m_\text{X} \text{ mol kg}^{-1}$. The several equivalent measures of abundance are presented in Table 2.1.

Table 2.1 Expressions for molar abundance of cloudwater dissolved species. Cloud liquid water volume fraction, L ; molality of dissolved species, $m_\text{X} \text{ mol kg}^{-1}$

Quantity	Unit	Symbol	Expression
Concentration	mol m^{-3}	C_X	$L m_\text{X}$
Partial pressure	Pa	\hat{p}_X^*	$L R_g T m_\text{X}$
Partial pressure	bar	p_X^*	$10^{-5} L R_g T m_\text{X}$
Mixing ratio	mol/mol (air)	x_X	$10^{-5} L R_g T m_\text{X} / \hat{p}_\text{air}(\text{bar})$

6 MASS ACCOMMODATION AND INTERFACIAL MASS-TRANSPORT RATES

Much attention has been paid in recent years to the measurement of mass accommodation coefficients of gaseous substances on the air–water interface and to the examination of the implication of such mass accommodation coefficients on the rate of uptake and reaction of gases in cloudwater. The mass accommodation coefficient is the fraction of collisions from the gas phase on to the solution interface that result in transfer of molecules from the gas phase to the liquid phase. Here we review the pertinent derivations and implications. The Henry's law coefficient is central to both.

Consider the flux of a species X from the gas phase into a solution. The collision rate ($\text{mol m}^{-2} \text{s}^{-1}$) is evaluated from the kinetic theory of gases as

$$\sigma_X^+ = \frac{1}{4} \alpha_X \bar{v}_X C_{X(g)}(0+) \quad (2.7)$$

where $\bar{v}_X = (8R_g T / \pi MW_X)^{1/2}$ is the mean molecular speed of the species X, α_X is the mass accommodation coefficient and $C_{X(g)}(0+)$ is the concentration of the species at the interface, on the gas side, which may differ appreciably from the bulk concentration because of a diffusive gradient in the vicinity of the interface. This flux can be expressed equivalently in terms of the hypothetical aqueous-phase concentration $C_{X(aq)}^*(0+)$ that would exist in equilibrium with the gas-phase concentration $C_{X(g)}(0+)$, as

$$\sigma_X^+ = \frac{1}{4} \alpha_X \bar{v}_X C_{X(aq)}^*(0+) / \tilde{H}_X$$

Here it is most convenient to use the dimensionless (concentration/concentration) Henry's law coefficient. The flux given by Equation (2.7) is a gross flux, which may be offset by a return flux from the solution phase into the gas phase. This return flux is

$$\sigma_X^- = \frac{1}{4} \bar{v}_X C_{X(aq)}(0-) / \tilde{H}_X$$

where $C_{X(aq)}(0-)$ denotes the concentration of the species at the interface, on the water side. This is so because, by microscopic reversibility, σ_X^- must be equal to σ_X^+ at phase equilibrium [i.e. when $C_{X(aq)}(0-) = \tilde{H}_X C_{X(g)}(0+)$] and because the flux scales linearly with the concentration. The net flux into solution is

$$\sigma_X \equiv \sigma_X^+ - \sigma_X^- = \frac{1}{4} \alpha_X \bar{v}_X [C_{X(g)}(0+) - C_{X(aq)}(0-) / \tilde{H}_X] \quad (2.8)$$

Equation (2.8) sets an upper limit to the mass transfer rate that must be considered in any treatment of interphase mass transfer; depending on the value of α_X , this may or may not present an appreciable limitation to the overall rate.

7 COUPLED MASS TRANSFER AND AQUEOUS-PHASE REACTION

This discussion (based on Schwartz [8]) develops expressions describing the rate of gas and aqueous-phase mass transport and aqueous-phase reaction. The

exchange flux of a gaseous species between the gas and aqueous phases may be described phenomenologically (e.g. Danckwerts [9]) as the product of an overall mass-transfer coefficient K_g times the difference between the gas-phase concentration $C_{X(g)}$ and the aqueous-phase concentration $C_{X(aq)}$ divided by the dimensionless Henry's law coefficient \tilde{H}_X describing the equilibrium solubility of the gas in the aqueous medium:

$$\sigma_X = K_g[C_{X(g)} - C_{X(aq)}/\tilde{H}_X] \quad (2.9)$$

where $C_{X(g)}$ and $C_{X(aq)}$ refer to concentrations in the 'bulk' of the phase, that is, at distances sufficiently far from the interface to be outside the region of strong gradient in the vicinity of the interface. For concentrations in units of mol m^{-3} , the flux has units $\text{mol m}^{-2} \text{s}^{-1}$. Note that here we use the dimensionless Henry's law coefficient \tilde{H}_X . This expression is fairly general, being applicable to a variety of situations of interest in atmospheric chemistry, for example to the uptake of a gas into cloudwater by uptake followed by aqueous-phase reaction or to dry deposition of a gas to surface water. All of the physics (and chemistry) of the mass-transfer process is embodied in the mass-transfer coefficient K_g ; the subscript g denotes that this is the gas-side mass transfer coefficient. This quantity has dimension of length/time, or velocity.

It is evident from Equation (2.9) that in order for there to be a net flux, the aqueous-phase concentration $C_{X(aq)}$ must not be in equilibrium with the gas-phase concentration $C_{X(g)}$, i.e. that $C_{X(aq)} \neq \tilde{H}_X C_{X(g)}$; more specifically, for there to be a net uptake in the aqueous medium $C_{X(aq)}$ must be less than $\tilde{H}_X C_{X(g)}$. The lack of equilibrium may be due to aqueous-phase chemical reaction depleting the concentration the dissolved gas or, alternatively, in the case of dry deposition to surface water, simply to the fact that the water is undersaturated relative to the atmospheric concentration of the gas, for example because of transfer from the mixed layer of the ocean to the deep ocean.

If the aqueous-phase concentration of the depositing substance $C_{X(aq)}$ is 0 [more precisely, if $C_{X(aq)} \ll \tilde{H}_X C_{X(g)}$], then $\sigma_X = K_g C_{X(g)}$. However, the condition $C_{X(aq)} \ll \tilde{H}_X C_{X(g)}$ does not necessarily imply that the flux is equal to its maximum possible value, as governed by atmospheric mass transport only, since there may be a return flux (aqueous phase to gas phase) resulting from a near-interface aqueous-phase concentration that is substantial compared to $\tilde{H}_X C_{X(g)}$ even when $C_{X(aq)} \ll \tilde{H}_X C_{X(g)}$.

The choice of the gas-phase concentration, rather than the aqueous-phase concentration, as that to which to refer the flux is arbitrary, reflecting the gas-phase orientation of atmospheric chemists. The flux might entirely equivalently be referred to the aqueous-phase concentration, viz.

$$\sigma_X = K_l[\tilde{H}_X C_{X(g)} - C_{X(aq)}]$$

where K_l is referred to as the liquid-side mass transfer coefficient; it is seen that $K_l = K_g/\tilde{H}_X$.

Considerable progress is made in understanding and describing the overall mass-transfer process by considering it to be a sequence of processes, from the bulk gas phase to the interface, across the interface, and from the interface to the bulk aqueous phase. These fluxes are described, respectively, as

$$\sigma_X = k_g[C_{X(g)} - C_{X(g)}(0+)] \quad (2.10)$$

$$\sigma_X = \frac{1}{4}\alpha_X\bar{v}_X[C_{X(g)}(0+) - C_{X(aq)}(0-)/\tilde{H}_X] \quad (2.8)$$

$$\sigma_X = \beta k_L(C_{X(aq)}(0-) - C_{X(aq)}) \quad (2.11)$$

where $C_{X(g)}(0+)$ denotes the concentration of the species at the interface, on the gas side, which may differ appreciably from the bulk gas-phase concentration because of a diffusive gradient in the vicinity of the interface; likewise, $C_{X(aq)}(0-)$ denotes the concentration of the species at the interface, on the water side. The gas-phase and liquid-phase mass-transfer coefficients k_g and k_l describe *physical* mass transfer (turbulent diffusion plus molecular diffusion through the laminar boundary layer immediately adjacent to the interface); the magnitudes of these coefficients depend on the degree of physical agitation characterizing the system. The coefficient β , to be discussed later, represents enhancement of the aqueous-phase mass-transfer flux due to removal of the material by chemical reaction; when there is no enhancement, $\beta = 1$.

Under steady-state conditions the flux is constant and equal in both media and across the interface. By equating the several expressions for the flux [Equations (2.8)–(2.11)], one obtains the overall mass-transfer coefficient as the inverse sum of the mass-transfer coefficients in the two media and at the interface:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{(\frac{1}{4})\bar{v}_X\alpha_X} + \frac{1}{\tilde{H}_X k_L \beta} \quad (2.12)$$

In the absence of any aqueous-phase chemical reaction of the dissolved gas that would enhance the rate of uptake, the enhancement coefficient β is equal to unity. This corresponds to the two-film expression commonly employed in evaluating air–sea fluxes of nonreactive gases (e.g. [10]). Under the assumption that the interfacial resistance is negligible, then there is a critical solubility $\tilde{H}_{crit} \equiv k_g/k_l$ for which the gas- and liquid-phase resistances are equal. For $\tilde{H} \ll \tilde{H}_{crit}$, liquid-phase mass transport is controlling and the uptake rate is linearly dependent on \tilde{H} . For $\tilde{H} \gg \tilde{H}_{crit}$, gas-phase mass transport is controlling and the uptake rate is independent of \tilde{H} . For reactive gases the effect of the chemical removal process is exhibited in the enhancement coefficient β , and it is $\beta\tilde{H}$ that is to be compared with \tilde{H}_{crit} .

To examine reactive enhancement of uptake, it is necessary to model the concurrent mass-transfer and reactive processes, and a number of models have been introduced over the years, largely in the chemical engineering literature. The most familiar such model is the so-called diffusive-film model, which posits an unstirred laminar film at the interface having thickness D_X^{aq}/k_l , where D_X^{aq} is the molecular diffusion coefficient of the dissolved gas in aqueous solution.

The reactive gas must diffuse through this film to the bulk convectively mixed liquid. Reaction occurs in the film and/or in the bulk liquid depending on the relative rates of reaction and mass transport. Although criticized as unrealistic, this model has received widespread application in the geochemical literature. Alternative models posit systematic or stochastic transport of stagnant, near-surface parcels of liquid into the bulk, again with reaction occurring to greater or lesser extent in these unstirred parcels depending on the relative rates of reaction and mass transport. In all cases the liquid-phase mass transport is characterized by the single parameter k_1 as well as by D_X^{aq} .

Rates of reactive uptake for the three models were examined and compared by Danckwerts and Kennedy [11]. For the diffusive film model the expression for β for a reversible first-order reaction of the dissolved gas can be written as

$$\beta = \frac{\eta}{1 + (\eta - 1) \left(\frac{\tanh \kappa^{\frac{1}{2}}}{\kappa^{\frac{1}{2}}} \right)} \quad (2.13)$$

where η is the ratio at equilibrium of the total concentration of dissolved material to the concentration given by Henry's law dissolution alone, $\eta = \tilde{H}_X^*/\tilde{H}_X$, and κ is a dimensionless rate coefficient for reaction,

$$\kappa = \frac{k_{\text{aq}}^{(1)}}{k_1^2/D_X^{\text{aq}}} \cdot \frac{\eta}{\eta - 1} \quad (2.14)$$

where $k_{\text{aq}}^{(1)}$ is the effective first-order rate coefficient for aqueous-phase reaction of the dissolved gas.

A few words should be said about the factors $\eta/(\eta - 1)$ and k_1^2/D_X^{aq} employed in the definition of κ . At $\eta \gg 1$, which corresponds to large equilibrium enhancement of the solubility and which is often the situation of interest for reactive uptake, $\eta/(\eta - 1) \approx 1$ and this factor can thus be neglected in evaluation of κ . At low values of η (recall that $\eta \geq 1$) the factor $\eta/(\eta - 1)$ gives rise to substantial enhancement of κ essentially because the reaction does not need to proceed very far to reach equilibrium. The quantity $k_{\text{crit}} \equiv k_1^2/D_X^{\text{aq}}$ has dimension of inverse time; comparison of $k_{\text{aq}}^{(1)}$ with k_{crit} permits the importance of reactive enhancement to the rate of uptake to be immediately assessed.

Despite somewhat different and more realistic assumptions of the surface renewal models, these models were found to yield expressions for β that differ from Equation (2.13) by no more than a few percent [11]. These models have gained substantial support in laboratory studies (e.g. [9]). Expressions for the kinetic enhancement equivalent to Equation (2.13) were later obtained in the context of atmosphere-surface water exchange by Bolin [12] and by Hoover and Berkshire [13] and are sometimes associated with those investigators.

Although all that remains to evaluate β (and ultimately K_g) is knowledge of the pertinent parameters, it is worthwhile to examine the dependence of the enhancement of uptake on the equilibrium constant and reaction rate constant.

At low values of the argument (≤ 0.5), i.e. for low reaction rate coefficients, the hyperbolic tangent function \tanh closely approximates the argument itself, so that $\tanh \kappa^{1/2} / \kappa^{1/2}$ approaches unity and in turn β approaches unity. Thus approximately (within 10 %)

$$\beta \approx 1 \quad \text{for } \kappa \leq 0.3 \quad (12.13a)$$

In this limiting situation there is essentially no enhancement of the rate of uptake over that given by physical dissolution alone. For somewhat greater values of κ , where the enhancement becomes appreciable, β is approximated by series expansion of the \tanh function (again within 10 %) as

$$\beta \approx 1 + \frac{1}{3} \frac{\eta - 1}{\eta} \kappa = 1 + \frac{1}{3} \frac{k_{aq}^{(1)}}{k_l^2 / D_{Xaq}} \quad \text{for } \kappa \leq 2.1 \quad (2.13b)$$

At the other extreme, for values of the argument of \tanh greater than about 1.5 (i.e. at high reaction rates), \tanh approaches unity, and to good approximation

$$\beta \approx \frac{\eta}{1 + \frac{\eta - 1}{\kappa^{1/2}}} \equiv \frac{\kappa^{1/2}}{1 + \frac{\kappa^{1/2} - 1}{\eta}} \quad \text{for } \kappa \geq 2.4 \quad (2.13c)$$

For values of κ such that $(\kappa^{1/2} - 1) \ll \eta$, this expression simplifies to

$$\beta \approx \kappa^{1/2} \quad \text{for } 2.4 \leq \kappa \leq (1 + 0.1\eta)^2 \quad (2.13d)$$

Finally, if $\kappa^{1/2}$ is sufficiently great, the first term in the denominator of Equation (2.13) predominates and

$$\beta \approx \eta \quad \text{for } \kappa \geq 2.4 \text{ and } \kappa \geq 100(\eta - 1)^2 \quad (2.13e)$$

In this limit the rate of uptake is equal to that for a nonreactive gas whose solubility is enhanced, owing to instantaneous chemical equilibrium, by the factor η . This limit justifies the use of an effective Henry's law coefficient $k_{H_X}^* \equiv \eta k_{H_X}$ for rapidly established equilibria and specifies the range of applicability of this treatment.

The dependence of β on the effective first-order rate coefficient for reaction $k_{aq}^{(1)}$ is illustrated in Figure 2.2 for a range of values of η . The plateauing of β for large values of $k_{aq}^{(1)}$ and intermediate values of η corresponds to the limit in Equation (2.13e). The linear region of the graphs (slope = 0.5 on the logarithmic plot) corresponds to the limit in Equation (2.13d). This is equivalent to the well known [9] expression for diffusion controlled reaction for $\eta \gg 1$:

$$\beta k_l \approx [k_{aq}^{(1)} D_{Xaq}]^{1/2} \quad \text{for } 2.4 \leq \kappa \leq (1 + 0.1\eta)^2 \quad (2.15)$$

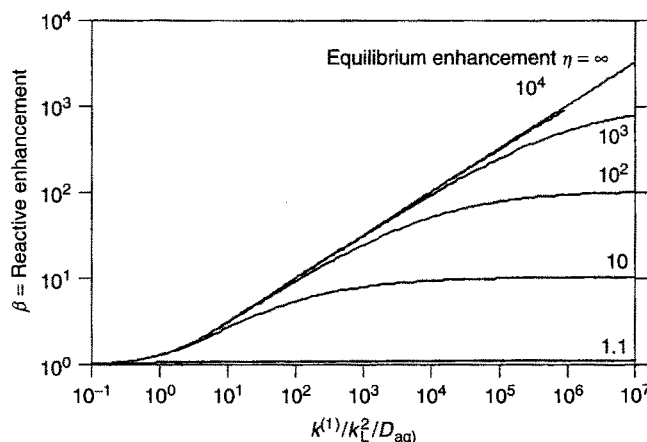


Figure 2.2 Dependence of the kinetic enhancement factor β of the aqueous-phase mass-transfer coefficient k_L as a function of the effective first-order rate constant for reaction, $k^{(1)}$, normalized to k_L^2/D_{aq} , where D_{aq} is the aqueous-phase molecular diffusion coefficient, for indicated values of the equilibrium solubility enhancement factor η (adapted from Schwartz [8])

8 RATES OF MULTI-PHASE REACTIONS IN LIQUID WATER CLOUDS

It is desired to evaluate the rate of aqueous-phase reactions in cloudwater under the assumption of solution equilibrium of the dissolved reacting gas and to express this reaction rate in units such that it can be compared with rates of gas-phase reactions. We take the cloud liquid water content L such that the liquid water volume fraction $L/\rho_{cw} \ll 1$ and assume Henry's law equilibrium; this assumption can be examined as outlined below by consideration of mass-transfer rates relative to the rate of reaction.

For a first-order aqueous-phase reaction having rate coefficient $k_{aq}^{(1)}$ (s^{-1}), the rate of aqueous-phase reaction ($\text{mol kg}^{-1} s^{-1}$) of a species X having molality $m_{X(aq)}$ (mol kg^{-1}) is

$$R_{X(aq)} = k_{aq}^{(1)} m_{X(aq)} = k_{Hx} k_{aq}^{(1)} p_X \quad (2.16)$$

Equivalent expressions for this rate are readily obtained from Table 2.1. In particular, the rate of reaction expressed in terms of partial pressure of the reagent gas p_X (Pa) is

$$\left(-\frac{d\hat{p}_X}{dt} \right)_{aq \text{ rxn}} = L R_g T R_{X(aq)} = L R_g T k_{aq}^{(1)} \hat{k}_{Hx} \hat{p}_X$$

from which the effective first-order loss rate coefficient for this process referred to the total amount of material X in the volume $\gamma_{X,aq}$ (unit: s^{-1}) is

$$\gamma_{X,aq} \equiv \frac{1}{(\hat{p}_X + \hat{p}_X^*)} \left(-\frac{d\hat{p}_X}{dt} \right)_{aq \text{ rxn}} = L R_g T \hat{k}_{Hx} k_{aq}^{(1)} \frac{\hat{p}_X}{\hat{p}_X + \hat{p}_X^*}$$

For a gaseous reagent species predominantly present in the gas phase, $\hat{p}_X \gg \hat{p}_X^*$ and we obtain the result

$$\gamma_{X, \text{aq}} \equiv \frac{1}{(p_X + p_X^*)} \left(-\frac{dp_X}{dt} \right)_{\text{aq rxn}} = L R_g T \hat{k}_{H_X} k_{\text{aq}}^{(1)} = 10^{-5} L R_g T \hat{k}_{H_X} k_{\text{aq}}^{(1)}$$

This important quantity may be readily evaluated for known aqueous-phase first-order reaction rate coefficient $k_{\text{aq}}^{(1)}$. $\gamma_{X, \text{aq}}$ scales linearly with liquid water content, Henry's law coefficient, and aqueous-phase rate constant. It may be readily and immediately compared with the rate coefficient for gas-phase reaction of species X and thus provides the means of comparing rates of gas- and aqueous-phase reactions of a given species.

For other than first-order reaction, $k_{\text{aq}}^{(1)}$ is replaced by the effective first-order reaction rate coefficient, evaluated, for example, as the product of second-order reaction rate coefficient and concentration of other reacting species.

9 DEPARTURE FROM PHASE EQUILIBRIUM AT AIR-WATER INTERFACE

For a given flux into the aqueous phase, corresponding to an assumed reaction rate, the fractional departure from equilibrium at the interface can be evaluated to examine for mass-transport limitation to the rate of reaction as a function of measured or specified mass accommodation coefficient and reaction rate [13]. This fractional departure is

$$\frac{\tilde{H}_X C_{X(g)}(0+) - C_{X(aq)}(0-)}{\tilde{H}_X C_{X(g)}(0+)} = \frac{\sigma_X}{\alpha_X \bar{v}_X C_{X(g)}(0+)/4} = \frac{\sigma_X}{\alpha_X \bar{v}_X \hat{p}_{X(g)}(0+)/4 R_g T} \quad (2.17)$$

Note that here the partial pressure of the gas is in units of Pa. Particular attention must be paid here to consistency of units or else errors can result (e.g. Ref. 9 p. 69); a major strength of SI is that such consistency is intrinsic.

Following Schwartz [14], we may use Equation (2.17) to test whether the rate of reaction in a spherical drop is appreciably limited by the rate of interfacial mass transport. For departure from phase equilibrium not to exceed a criterion, arbitrarily taken as 10 %,

$$\sigma_X \leq 0.1 \frac{\alpha_X \bar{v}_X \hat{p}_{X(g)}(0+)}{4 R_g T}$$

For a spherical drop of radius a , the flux σ_X corresponds to an uptake rate $4\pi a^2 \sigma_X$ or a mean volumetric reaction rate $\bar{R}_{X(aq)} = (4\pi a^2 \sigma_X)/(4\pi a^3/3) = 3\sigma_X/a$, whence the criterion that must be satisfied for mass transport limitation not to exceed 10 % is

$$\bar{R}_{X(aq)} \leq 0.1 \frac{\alpha_X \bar{v}_X \hat{p}_{X(g)}(0+)}{(4/3)a R_g T}$$

For the aqueous-phase reaction rate given by Equation (2.16) this criterion becomes

$$\hat{k}_{\text{H}_X} k_{\text{aq}}^{(1)} \leq 0.1 \frac{\alpha_X \bar{v}_X}{(4/3)aR_g T} \text{ or } k_{\text{H}_X} k_{\text{aq}}^{(1)} \leq 10^4 \frac{\alpha_X \bar{v}_X}{(4/3)aR_g T}$$

Note that here, as in general where the Henry's law coefficient appears in expressions, we must use the Henry's law coefficient in strict SI units, i.e. $\text{mol kg}^{-1} \text{Pa}^{-1}$. In the second form of the criterion this Henry's law coefficient has been replaced by that in $\text{mol kg}^{-1} \text{bar}^{-1}$ units.

A similar expression has been given by Schwartz [14] as a criterion for absence of limitation to the rate of multi-phase reaction due to the finite rate of gas-phase diffusion, viz.

$$\hat{k}_{\text{H}_X} k_{\text{aq}}^{(1)} \leq 0.1 \frac{3D_g}{a^2 R_g T} \text{ or } k_{\text{H}_X} k_{\text{aq}}^{(1)} \leq 10^4 \frac{3D_g}{a^2 R_g T}$$

10 DRY DEPOSITION OF GASES TO SURFACE WATER

As presented above, the flux of dry deposition of atmospheric gases to surface water, or more generally the exchange flux between the atmosphere and surface water, may be evaluated for known values of the pertinent mass-transfer coefficients in the two phases and the Henry's law coefficient, taking into account any reactive enhancement. Dry deposition is generally expressed as the product of the atmospheric concentration times a deposition velocity v_d :

$$\sigma_X = v_d C_{X(g)}$$

whence $v_d = K_g$ provided that $C_{X(aq)} \ll \tilde{H}_X C_{X(g)}$.

Here we examine the dependence of deposition velocity on the several parameters. An approximate value for k_g is 0.13 % of the wind speed, for a reference height of 10 m; the exact proportionality coefficient depends somewhat on the reference height and on the atmospheric stability [15]. Thus, for typical wind speeds of 3–15 m s^{-1} , values of k_g range from 4 to 20 mm s^{-1} . An expression for k_l given by Liss and Merlivat [16], which exhibits three linear regions of dependence on wind speed (increasing slope with increasing wind speed), has gained substantial support (e.g. [17]). That expression gives $k_l = 1.4 \times 10^{-6}$, 1.3×10^{-5} and $1.1 \times 10^{-4} \text{ m s}^{-1}$ for wind speeds of 3, 5 and 10 m s^{-1} , respectively; the actual values depend somewhat on the identity of the transported gas and on temperature. We take these values as representative of the range that must be considered for the present purpose of identifying factors governing dry deposition of gases to surface waters. However, it must be stressed that although these values are representative, the problem of specifying the precise values pertinent to a given environmental situation is by no means solved.

Figure 2.3 shows the overall mass-transfer coefficient K_g in the absence of reactive enhancement as a function of Henry's law coefficient for representative values of k_l and k_g . Also shown are values of Henry's law and effective Henry's law coefficients for several gases of atmospheric interest. The points marked by • represent the equilibrium solubility after the reaction (acid–base dissociation,

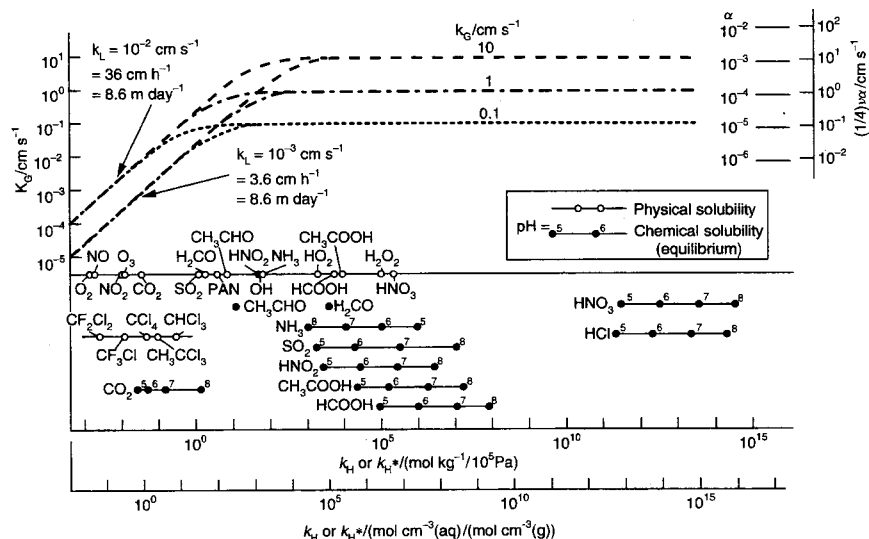


Figure 2.3 Overall mass-transfer coefficient K_G (in the absence of interfacial mass-transport limitation) for nonreactive gases ($\beta = 1$) as a function of solubility for values of k_G and k_L indicated on the asymptotes of the curves. The scale at the right permits comparison of interfacial and overall conductance for indicated values of the mass-accommodation coefficient α . Also shown are Henry's law coefficients k_H (open circles) and effective Henry's law coefficients k_H^* (filled circles) of a number of atmospheric gases; the intermediate abscissa scale gives k_H and k_H^* in units of $\text{mol kg}^{-1}/(10^5 \text{ Pa})$ (adapted from Schwartz [8])

pH dependent, or aldehyde hydrolysis) has gone to completion; the ratio to the physical solubility (indicated by \circ) gives the equilibrium enhancement factor η . The thrust of the figure is that without reactive enhancement there are few gases that are sufficiently soluble in water that for representative values of k_g and k_l their deposition velocity would be controlled by atmospheric mass transport. This figure demonstrates the important influence of reactive enhancement on k_l .

A further feature of the figure is the device at the upper right, which displays the interfacial conductance, evaluated as $(1/4)\bar{v}\alpha$, for indicated values of the mass-accommodation coefficient α . Here the mean molecular speed, which depends on molecular weight, has been taken as $4 \times 10^2 \text{ m s}^{-1}$. Interfacial resistance to mass transport should be taken into consideration if interfacial conductance is comparable to K_g evaluated with only the gas- and liquid-phase resistances. Interfacial resistance is not limiting to the rate of dry deposition for values of $\alpha \gtrsim 10^{-4}$ but, depending on the value of K_g evaluated with only the gas- and liquid-phase resistances, might become limiting for lower values of α .

11 CONCLUSIONS

Exchange of volatile species between the gas phase of the atmosphere and liquid water is a key process in the evolution of materials in the earth's environment

system. The driving force for this exchange is the Henry's law solubility equilibrium together with rapid equilibria in aqueous solution. The Henry's law constant, or the effective Henry's law constant that takes these rapid equilibria into account, is thus a fundamental property of volatile atmospheric species in the earth's environment that must be well known in order to describe the extent and rate of these phenomena under circumstances of interest. The Henry's law constant (or effective Henry's law constant) ranges fairly widely for substances of interest to the earth's atmospheric environment, by some 18 orders of magnitude. Because of this wide range of solubilities, the rates and extents of various processes, such as the distribution between gas and liquid phase in clouds, likewise vary substantially. In many situations it is sufficient to identify limiting cases applicable to sparingly soluble or highly soluble gases. For example, the zeroth-order question is where the bulk of the material resides, and often knowledge of this is sufficient for the task at hand, for which an order of magnitude estimate of the solubility is often sufficient. Clearly insoluble gases such as nitrogen and oxygen are present essentially entirely in the gas phase. Very soluble material, such as nitric acid, would be expected to be present essentially entirely in the liquid phase, at least for clouds of sufficient liquid water content. In some instances it is necessary to know the amount of material present in the lesser compartment, for example in the calculation of the rate of aqueous phase reactions in cloudwater. These calculations require rather precise knowledge of the Henry's law solubility.

This chapter has presented formalism to describe several applications of Henry's law solubility to atmospheric chemistry. It is hoped that it provides a sense of the pertinence and use of solubility data in atmospheric chemistry and will stimulate interest in the evaluated Henry's law data presented in this volume.

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